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Original article

In situ synthesis of a spherical covalent organic framework as a stationary phase for capillary electrochromatography

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ABSTRACT

Covalent organic frameworks (COFs) are a novel type of crystalline porous organic polymer materials recently developed. It has several advantages in chromatographic separation field, such as high thermal stability, porosity, structural regularity, and large specific surface area. Here, a novel spherical COF 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde (BPTA) was developed as an electrochromatographic stationary phase for capillary electrochromatography separation. The COF TAPB-BPTA modified capillary column was fabricated via a facile in situ growth method at room temperature. The characterization results of scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, and X-ray diffraction (XRD) confirmed that COF TAPB-BPTA were successfully modified onto the capillary inner surface. The electrochromatography separation performance of the COF TAPB-BPTA modified capillary was investigated. The prepared column demonstrated outstanding separation performance toward alkylbenzenes, phenols, and chlorobenzenes compounds. Furthermore, the baseline separations of non-steroidal anti-inflammatory drugs (NSAIDs) and parabens with good efficiency and high resolution were achieved. Also, the prepared column possessed satisfactory precision of the intra-day runs ($n = 5$), inter-day runs ($n = 3$), and parallel columns ($n = 3$), and the relative standard deviations (RSDs) of the retention times of tested alkylbenzenes were all less than 2.58%. Thus, this new COF-based stationary phase shows tremendous application potential in chromatographic separation field.

1. Introduction

Capillary electrophoresis (CE), a versatile analytical method, is used for separation and analysis in various fields, such as the separation of large biomolecules, neutral molecules, and small ions [1]. CE has developed in different separation modes, such as capillary electrochromatography (CEC), capillary gel electrophoresis, capillary zone electrophoresis, and capillary electrophoresis in microchip [2], based on the different properties and detection requirements of analytes. CEC has high column efficiency of CE and high selectivity of high performance liquid chromatography (HPLC). Therefore, it has attracted extensive attention and developed rapidly. The CEC column, which is divided into three types: packed column, monolithic column, and open tubular (OT) column, is the essential component of CEC. In OT-CEC, the stationary phase is connected with the inner walls of the capillary by coating, physical adsorption, and chemical bonding. It shows great superiority of simple preparation, good permeability, good reproducibility, stable electroosmotic flow, and simple experiment. It has been successfully applied in various fields, including food analysis [3], drug analysis, and chiral separation [4–8].

Exploring the appropriate stationary phases to apply in CEC is the core topic of OT-CEC. Recently, various porous or nanomaterials have been investigated as OT-CEC stationary phases [9,10], such as graphene oxide [10,11], magnetic nanoparticles [12], metal-organic frameworks (MOFs) [6,7,13], porous organic molecular cages [14] and covalent organic frameworks (COFs) [15–20]. However, OT

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columns have a low phase ratio, which may result in poor separation performance.

COFs are intriguing crystalline porous network materials that connect organic structural units through covalent bonds to form layered or network structures [21–24]. In particular, they have the advantages of high thermal stability, porosity, structural regularity, designable structures, and large specific surface area [24,25]. Therefore, COFs are widely applied in gas storage fields [26], photoelectrochemistry [24,27], adsorption [28], catalysis [29], biomedical application [30], and especially separation science [31–34]. Various COFs have been introduced via different preparation methods as stationary phases for OT-CEC separation [15–20,35,36]. Among them, the in situ room temperature synthesis technique is quite facile, green, and easy to control, which has recently sparked interest. For instance, Fu et al. [35] presented the in situ growth of COF 1,3,5-Tris-(4-formylphenyl)benzene (TFPB)-benzidine (BD) as a stationary phase for OT-CEC separation at room temperature. The obtained capillary column showed excellent performance in the separation of alkylbenzenes, chlorobenzenes, and phenolic compounds. Another work of our group [36] described the in situ room temperature synthesis of a COF 4,4′,4′′-(1,3,5-triazine-2,4,6-triyl)trianiline (Tz)-1,4-dihydroxyterephthalaldehyde (Da) onto the capillary inner surface for electrochromatographic separation of small neutral compounds, acidic and basic compounds, and food additives, etc.

Here, a novel spherical COF 1,3,5-tris(4-aminophenyl)benzene (TAPB)-2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde (BPTA) with good stability and porosity was used as the electrochromatographic stationary phase for OT-CEC. The results of scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectra, and X-ray diffraction (XRD) showed that COF TAPB-BPTA was successfully modified on the inner wall of the capillary. The CEC separation performance of the prepared TAPB-BPTA modified OT column was evaluated. The resulting columns showed prominent electrochromatographic separation performance toward alkylbenzenes, phenols, chlorobenzene compounds, nonsteroidal anti-inflammatory drugs, and parabens. The highest theoretical plate number was 1.78×10^5 plates/m (for methylparaben). Additionally, the TAPB-BPTA modified column showed excellent repeatability and stability.

2. Experimental

2.1. Reagents and instrumentation

2.1.1. Reagents and materials

Propylparaben, chlorobenzene, 1,2,4-trichlorobenzene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, 3-aminopropyltriethoxysilane (APTES), phenol, 2,4-dimethylphenol, 2,4-dichlorophenol and glutaraldehyde solution (25%, *V*/*V* in water) were obtained from Aladdin Reagent Factory (Shanghai, China). Methylbenzene, 1,2-dichlorobenzene, sodium hydroxide (NaOH), thiourea, 1,4-dioxane, hydrochloric acid (HCl), sodium phosphate dibasic dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), and acetic acid (CH_3COOH) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). Methylparaben and TAPB were obtained from Bidepharm (Shanghai, China). Ethylparaben, ibuprofen, and BPTA were purchased from Mackin (Shanghai, China). Flurbiprofen was purchased from HEOWNS (Tianjin, China). Diclofenac sodium was obtained from TCI (Shanghai, China). Phosphoric acid (H_3PO_4) was purchased from RHAWN (Shanghai, China). Acetonitrile and methanol were obtained from Tedia (Cincinnati, Ohio, USA). Fused silica capillaries (50 μm i.d. and 365 μm o.d.) were purchased from Ruifeng Chromatographic Devices (Yongnian, Hebei, China).

2.1.2. Instrumentation

All CEC separations were completed on an Agilent 7100 CE system (Waldbronn, Germany). The chromatographic workstation provided the data acquisition and treatment. The solutions through capillaries were pushed by a mechanical syringe pump (Longer Pump Company, Baoding, China). Ultrapure water was produced by a Milli-Q ultrapure water system (Waltham, MA, USA). Mettler-Toledo pH meter (Shanghai, China) was used to adjust the buffer pH values. A Carl Zeiss Ultra Plus Field (Oberkochen, Germany) acquired SEM images. FT-IR characterization was obtained from a Thermo NICOLET 5700 FT-IR spectrometer (Waltham, MA, USA).

2.2. Sample solutions and CEC experiments

The standard sample solutions of thiourea, methylbenzene, ethylbenzene, propylbenzene, butylbenzene, chlorobenzene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene were prepared at 4.0 mg/mL. Ibuprofen, flurbiprofen, and diclofenac sodium were dissolved to a standard solution of 3.0 mg/mL, respectively. The standard solutions of methylparaben, ethylparaben, propylparaben, phenol, 2,4-dimethylphenol, and 2,4-dichlorophenol were 3.0 mg/mL. All the analytes were dissolved in methanol. The phosphate buffer (PB; 10 mM) was prepared by dissolving sodium phosphate dibasic dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$) in ultrapure water. The pH values of PB were adjusted from 2.0 to 9.0 by adding phosphoric acid diluent. All standard solutions were stored in a refrigerator at 4 °C before use.

The mobile phase was composed of different proportions of acetonitrile (ACN) and PB before CEC runs. The injected sample solutions were obtained by diluting the standard solutions of analytes with the mobile phase. The prepared capillary column was then flushed with the mobile phase to equilibrate it until the baseline became stable. The sample solution was then injected using a pressure injection, and the separation was implemented with a voltage drive at 25 °C. After each run, the prepared capillary column was washed by the mobile phase for 120 s. Finally, the daily CEC experiment was completed, and the prepared capillary column was washed with methanol for 0.5 h, then dried by N_2 steam for further use.

2.3. Preparation of TAPB-BPTA modified capillary column

Fig. 1 shows the TAPB-BPTA modified capillary column preparation technique. First, the untreated capillary was rinsed with 1.0 M NaOH for 1 h, H_2O for 0.5 h, 1.0 M HCl for 1 h, H_2O for 0.5 h, and methanol for 0.5 h to expose the silicon hydroxyl group inside the capillary. Then, the capillary was dried using N_2 steam for 1 h for further use. The capillary column was cut to about 80 cm before the subsequent steps. Then the capillary column was full of the APTES solution, which was prepared by diluting APTES in water (10%, *V*/*V*). After sealing both ends of the capillary, it was placed in 95 °C water bathing for 0.5 h to obtain the amino group modified capillary. Then it was flushed with H_2O for 1 h and dried using N_2 steam for subsequent steps. The glutaraldehyde solution, made up of glutaraldehyde solution (25% (*V*/*V*) in H_2O) [37], was injected into the amino group modified capillary at 0.1 mL/h flow rate for 0.5 h at 25 °C. The aldehyde group modified capillary was obtained and then flushed with H_2O for 1 h and dried using N_2 steam for 1 h. Next, 2.0 mg/mL TAPB in 1,4-dioxane was enclosed in the capillary. Then the capillary column was placed in a 150 °C oil bath for 0.5 h. The TAPB modified capillary was rinsed with methanol for 1 h and dried using N_2 steam for 1 h for subsequent steps. The COF TAPB-BPTA synthesized solution was prepared according to the previous research with some changes [38]. TAPB (2.1 mg) and BTPA (2.18 mg) were accurately weighed out to be dissolved in 1 mL of ACN. It was rapidly injected into the TAPB modified capillary and sealed at both ends after adding 6 M of acetic acid (100 μL) as a

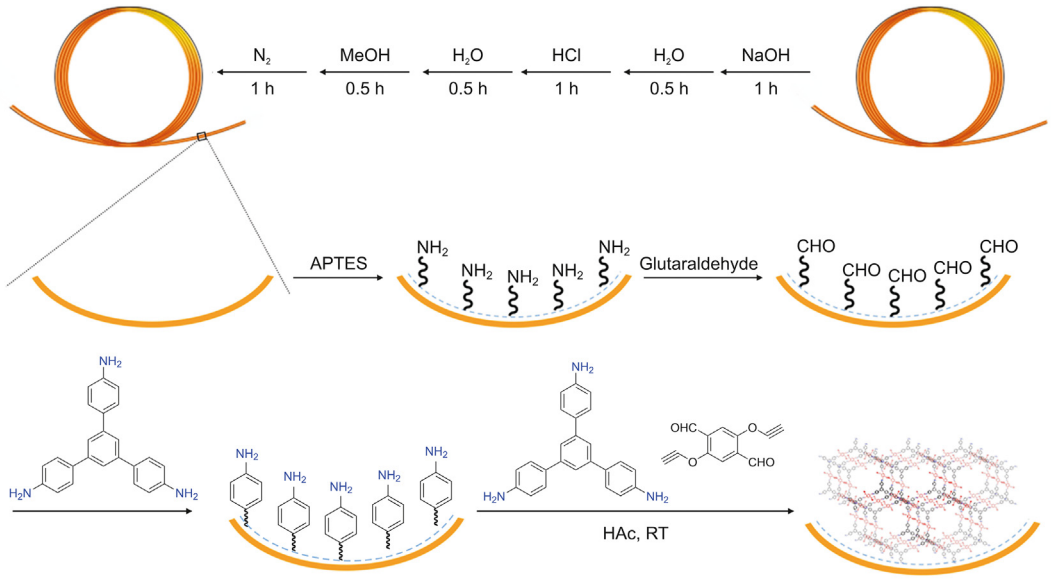

Fig. 1. Schematic procedure for the preparation of the covalent organic framework (COF) 1,3,5-tris(4-aminophenyl)benzene (TAPB)-2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde (BPTA) modified capillary. APTES: 3-aminopropyltriethoxysilane; HAc: acetic acid; RT: room temperature.

catalyst. After reaction at room temperature for 24 h, the capillary was rinsed with methanol for 1 h to remove unreacted substances and dried using N_2 steam. Then the TAPB-BPTA modified capillary was obtained. A mechanical syringe pump completed the above steps of flushing the capillary with water or methanol with a 0.05 mL/h flow rate. Finally, the total length of the TAPB-BPTA modified capillary in the CEC experiment was 35 cm, and the effective length was 26.5 cm.

3. Results and discussion

3.1. Characterizations

The morphology of the synthesized TAPB-BPTA was examined by SEM, and the images are shown in Figs. 2A and B. The SEM images of the polymer TAPB-BPTA particles showed small and uniform sphere, with a diameter of about 731.3 nm, which was

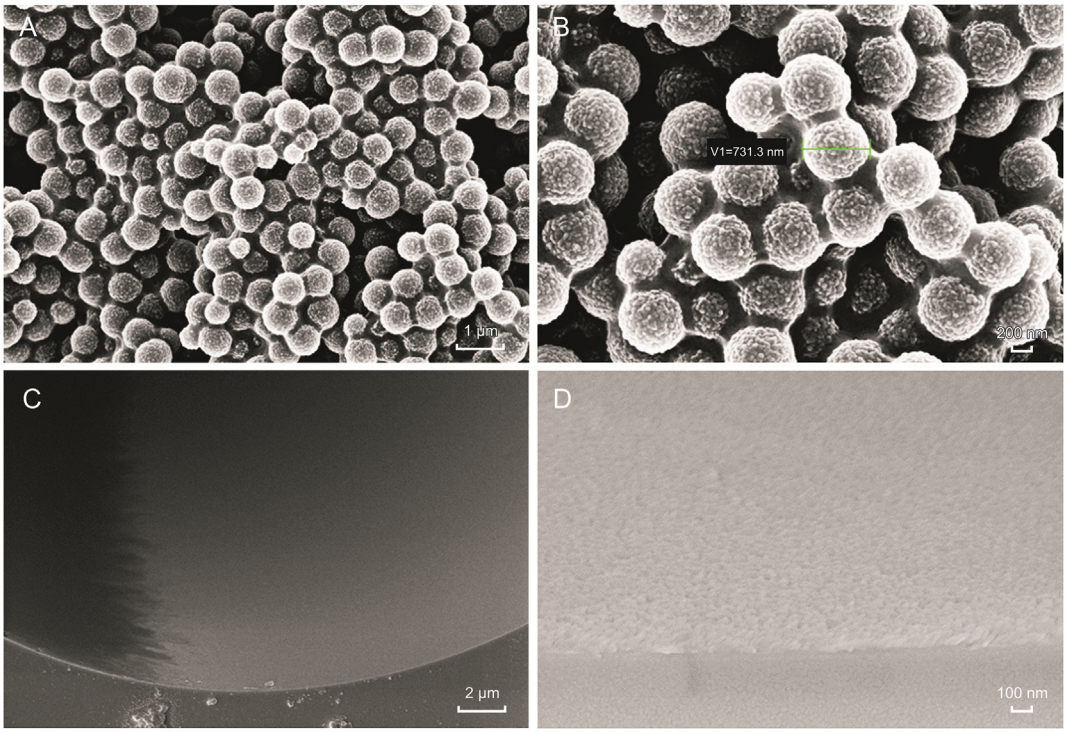

Fig. 2. Scanning electron microscopy (SEM) images of the as-synthesized COF TAPB-BPTA ((A) 10,000× and (B) 20,000×), (C) inner wall of bare capillary (50,000×), and (D) COF TAPB-BPTA modified capillary (50,000×).

consistent with the previously reported results [38]. Figs. 2C and D show the SEM images of the bare capillary and TAPB-BPTA modified capillary. The TAPB-BPTA modified capillary column showed a dense and uniform modified layer and an uneven surface compared with the bare capillary. The result confirmed the successful modification of TAPB-BPTA onto the capillary inner wall.

To confirm the successful modification of the TAPB-BPTA modified capillary, FT-IR and XRD were studied in detail. As shown in Fig. S1, a characteristic vibrational band of C=N at 1618 cm^{-1} appeared in the FT-IR spectrum of the TAPB-BPTA modified capillary, confirming the successful formation of imine-linked TAPB-BPTA on the capillary. The XRD results of the COF TAPB-BPTA and TAPB-BPTA modified capillary are shown in Fig. S2. The TAPB-BPTA modified capillary exhibited a weak peak at 2.8°. Overall, it can be concluded that TAPB-BPTA was successfully synthesized and modified onto the inner surface of the capillary.

3.2. Electroosmotic flow (EOF) evaluation experiment

EOF is important in CEC separation since it acts as the driving power. In this experiment, the EOF trend of prepared columns was investigated when the pH of the mobile phase changed from 2.0 to 5.0 under a specific voltage. The EOF is calculated as $\mu_{EOF} = (L_e \times L_t)/(U \times t_0)$, where L_e and L_t are the effective lengths and the total length of the column, respectively, U is the token of the application voltage, and t_0 is the EOF marker thiourea migration time. As shown in Fig. S3, with the pH value increasing from 2.0 to 5.0, the anode EOF mobility of the TAPB-BPTA modified capillary column decreased gradually. Theoretically, the positive charge of amino and imino groups is not affected under these evaluation conditions. When pH > 3, the uncovered hydroxyl group on the inner wall of the capillary begins to dissociate and take on a negative charge, resulting in cathodic EOF, which is partially offset by the anodic EOF generated by the amino groups. Therefore, with the increase of pH value, the degree of silanol dissociation increases, and the counteracting with reverse EOF increases, making the EOF of TAPB-BPTA modified capillary decrease.

3.3. Retention behavior

The TAPB-BPTA modified capillary column's retention mechanism was investigated. Thiourea (logP 1.05), toluene (logP 2.72), ethylbenzene (logP 3.23), propylbenzene (logP 3.73), and butylbenzene (logP 4.24) were selected as tested analytes. The calculation formula of retention factor (k) is $k = (t_r - t_0)/t_0$, where t_r and t_0 represent the retention time of four alkylbenzenes and the retention time of the EOF marker thiourea, respectively. The k of these four alkylbenzenes and the proportion of acetonitrile in the mobile phase are shown in Fig. S4. With the increased proportion of acetonitrile in the mobile phase from 25% to 50%, the retention factors of the four alkylbenzenes gradually decreased. Furthermore, it can be seen in Table S1 that the theoretical plates (N) increased, but the resolution decreased with the increase in acetonitrile content. Perspicuously, the increasing elution ability is due to the increase in acetonitrile content reduces resolutions and the decrease in peak broadening, and suggests a representative reversed-phase retention behavior of the TAPB-BPTA modified capillary.

3.4. Loading capacity

The loading capacity of a newly prepared capillary is defined as the sample injection amount when the corresponding half-height peak width ($W_{1/2}$) is increased by 10% compared to the $W_{1/2}$ of low sample volume [35,39]. The loading capacity of the TAPB-BPTA modified capillary was confirmed by injecting a series of toluene with different concentrations (0.2–1.2 mg/mL). Voltage injection was adopted to ensure the consistency of injection volume. Fig. S5 shows the relationship between the corresponding $W_{1/2}$ and toluene concentration. The $W_{1/2}$ of toluene at 0.9 mg/mL was 10.47% higher than the $W_{1/2}$ at 0.2 mg/mL. Therefore, the loading capacity of the TAPB-BPTA modified capillary column for toluene is 0.9 mg/mL, i.e., 68 pmol. The high loading capacity of the TAPB-BPTA modified capillary was probably because of the dense and uniform coating of TAPB-BPTA on the inner wall of the capillary, which offered a large surface area and sufficient interaction sites.

3.5. OT-CEC separation performance

Three series of neutral compounds, including alkylbenzenes, phenols, and chlorobenzenes, acted as model analytes in the CEC experiment to investigate the separation performance of the TAPB-BPTA modified capillary. As shown in Fig. 3, the methylbenzene (logP 2.720), ethylbenzene (logP 3.229), n-propylbenzene (logP 3.739), and n-butylbenzene (logP 4.248) were realized baseline separation and eluted in the order of the logP from small to large. Phenol (logP 1.540), 2,4-dimethylphenol (logP 2.496), and 2,4-dichlorophenol (logP 3.095) were also separated by the TAPB-BPTA modified capillary, as shown in Fig. 4, which achieved not only good separation effect but also the elution sequence consistent with its logP-value. Meanwhile, the separation result of chlorobenzene (logP 2.843), 1,2-dichlorobenzene (logP 3.444), and 1,2,4-trichlorobenzene (logP 4.102) is shown in Fig. 5. It realized baseline separation, and the elution sequence was also consistent with its logP-value. Therefore, the separation of these three groups of neutral compounds by the TAPB-BPTA modified capillary was mainly due to the hydrophobic interactions between the analytes and the COF coating layer on the capillary inner wall.

The TAPB-BPTA modified capillary was also used for drug separation and analysis. Ibuprofen (logP 3.502), flurbiprofen (logP 3.656), and diclofenac sodium (logP 4.120) are common nonsteroidal anti-inflammatory drugs (NSAIDs), and they also have some similarities in structure. Fig. 6A shows the separation results of these three NSAIDs. The complete separation of ibuprofen, flurbiprofen, and diclofenac sodium was obtained within 10 min. It can be seen that ibuprofen and flurbiprofen have similar logP values.

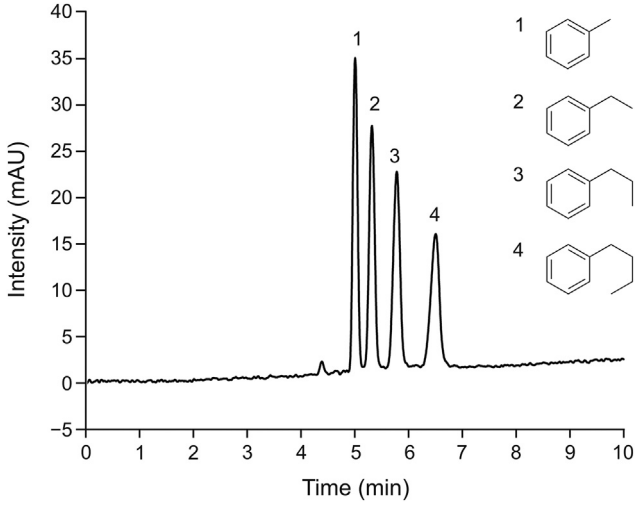

Fig. 3. Separation behavior of alkylbenzenes on the TAPB-BPTA modified capillary. Experimental conditions: mobile phase, 40% acetonitrile (ACN) in pH 3.0 10 mM phosphate buffer (PB); applied voltage, −15 kV; pressure injection, 40 mbar × 3 s; detection wavelength, 214 nm. 1: methylbenzene; 2: ethylbenzene; 3: n-propylbenzene; and 4: n-butylbenzene.

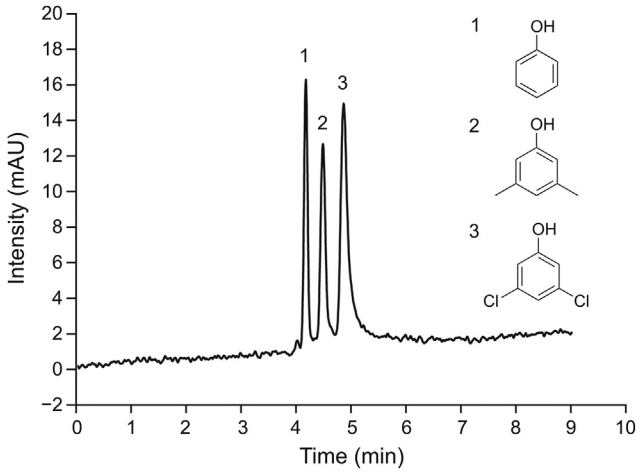

Fig. 4. Separation behavior of phenols on the TAPB-BPTA modified capillary. Experimental conditions: mobile phase, 27.5% ACN in pH 3.0 10 mM PB; applied voltage, −15 kV; pressure injection, 40 mbar × 4 s; detection wavelength, 210 nm. 1: phenol; 2: 2,4-dimethylphenol; and 3: 2,4-dichlorophenol.

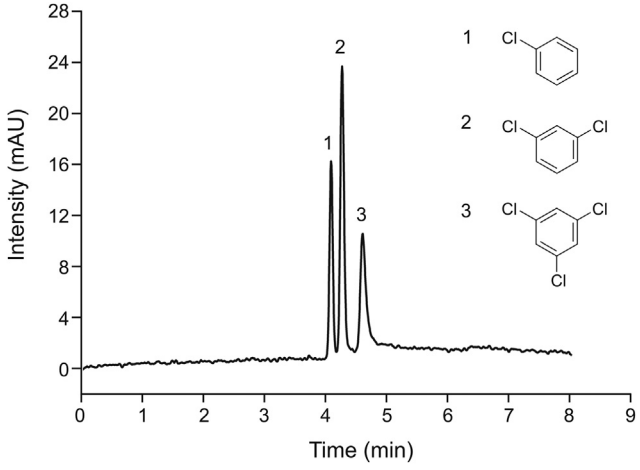

Fig. 5. Separation behavior of chlorobenzenes on the TAPB-BPTA modified capillary. Experimental conditions: mobile phase, 42.5% ACN in pH 3.0 10 mM PB; applied voltage, −15 kV; pressure injection, 50 mbar × 4 s; detection wavelength, 210 nm. 1: chlorobenzene; 2: 1,2-dichlorobenzene; and 3: 1,2,4-trichlorobenzene.

However, flurbiprofen was eluted later than ibuprofen. This was because flurbiprofen possessed more benzene rings than ibuprofen, thus enhancing the π-interaction between the COF coating layers. Hence, the separation of NSAIDs by the prepared column was mainly due to the π-interaction and hydrophobic interaction between analytes and the COF coating layer.

The TAPB-BPTA modified capillary can also be used to separate parabens. Taking methylparaben (logP 1.882), ethylparaben (logP 2.391), and propylparaben (logP 2.901) as separation targets, the separation result is shown in Fig. 6B, in which full baseline separation was obtained. The highest column efficiency (N) for methylparaben was 178,260 plates/m, indicating high-efficiency and resolution. The elution sequence was as follows: methylparaben < ethylparaben < propylparaben, which was consistent with the hydrophobicity of the analysis object. Additionally, the last peaks in most figures appeared to be tail and broadening. From Table S2, we can see that the theoretical plate numbers and symmetry factors decreased with the increase in the retention of tested compounds. This was mainly due to the stronger interaction between the analytes and the COF coating layer, which could prolong elution times and resulted in peak tailing and broadening. The above results showed the good applicability of the TAPB-BPTA modified capillary.

3.6. Reproducibility and stability

Reproducibility and stability are two important evaluation parameters for the newly developed OT-CEC columns. In this study, the reproducibility and stability of the TAPB-BPTA modified column were estimated using the relative standard deviations (RSDs) of the retention times of four alkylbenzenes. As shown in Table 1, the intra-day ($n = 5$) and inter-day ($n = 3$) RSDs of the retention times of the four alkylbenzenes were between 0.43%–0.66% and 1.91%–2.58%, respectively. Three batches of OT columns prepared in parallel were used to evaluate their column-to-column reproducibility, and the RSDs of the four alkylbenzenes were in the range of 1.34%–1.57%. Furthermore, after 50 injections, the TAPB-BPTA modified capillary separation performance did not change significantly. As shown in Fig. S6 and Table S3, it can still achieve good separation performance toward four alkylbenzenes without obvious retention time and peak shape changes. These results showed that the TAPB-BPTA modified capillary has good reproducibility and stability.

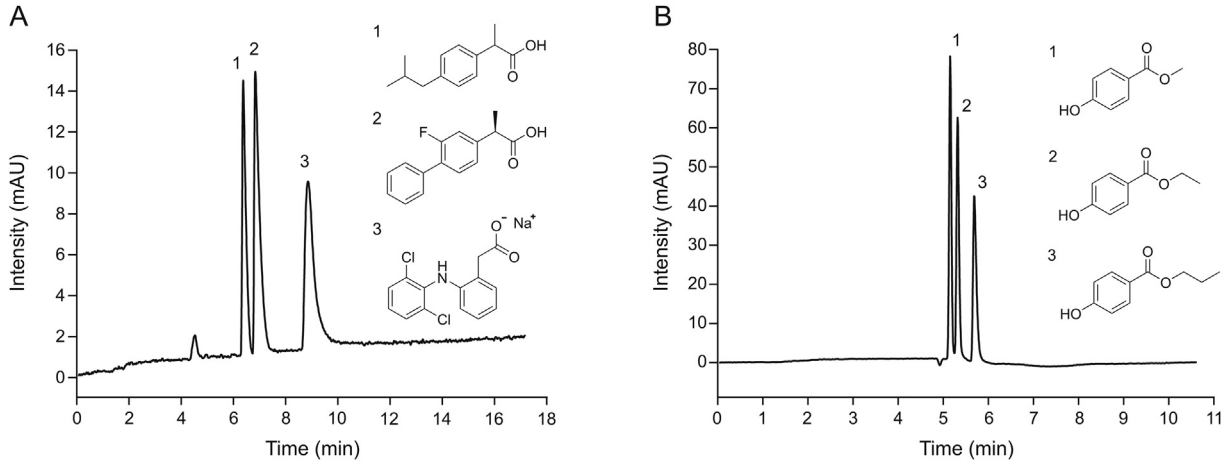

Fig. 6. Separation behavior of (A) non-steroidal anti-inflammatory drugs (NSAIDs) and (B) parabens on the TAPB-BPTA modified capillary. Experimental conditions: (A) mobile phase, 30% ACN in pH 3.0 10 mM PB; applied voltage, −20 kV; pressure injection, 50 mbar × 3 s; detection wavelength, 230 nm. 1: ibuprofen; 2: flurbiprofen; and 3: diclofenac sodium. (B) Mobile phase, 25% ACN in pH 3.0 10 mM PB; applied voltage, −15 kV; pressure injection, 20 mbar × 3 s; detection wavelength, 254 nm. 1: methylparaben; 2: ethylparaben; and 3: propylparaben.

Table 1
Reproducibility and stability of the 1,3,5-tris(4-aminophenyl)benzene (TAPB)-2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde (BPTA) modified capillary column.

Analytes	Retention time (RSD, %)		
	Intra-day ($n = 5$)	Inter-day ($n = 3$)	Column-to-column ($n = 3$)
Methylbenzene	0.58	2.58	1.34
Ethylbenzene	0.46	1.91	1.38
n-propylbenzene	0.43	2.04	1.57
n-butylbenzene	0.66	1.96	1.44

RSD: relative standard deviation.

Table 2
An overview of the reported methods for covalent organic frameworks (COFs)-based open tubular-capillary electrochromatography (OT-CEC) columns.

Materials	Methods	Analytes	Load capacity	Reproducibility (RSD, %)	The highest theoretical plate number (*N*, plates/m)	Refs.
COF-LZU-1	In situ synthesis	Neutral compounds, amino acids, and NSAIDs	–	<6.75 ($n = 3$)	–	[20]
COF-TFPB-BD	In situ synthesis	Neutral compounds, phenols, anilines, amino acids, and parabens	0.55 mg/mL (methylbenzene)	<2.83 ($n = 3$)	179,796 (phenol)	[35]
COF-LZU-1	Independent synthesis	Alkylbenzenes, anilines, and polyaromatic hydrocarbons	0.6 mg/mL (naphthalene)	<3.9 ($n = 3$)	129,237 (methylbenzene)	[39]
N_0-COF	Covalent bonding	Bisphenols and beverage	–	<8.53 ($n = 3$)	107,499 (BPF)	[40]
TpPa-1	Covalent bonding	Tetracyclines, sulfonamides, cephalosporins and amino acids	–	<4.9 ($n = 9$)	82,762 (tetracycline)	[41]
3D TpTAM	Covalent bonding	Fluoroquinolones and ciprofloxacin hydrochloride eye drops	–	<3.48 ($n = 3$)	137,608 (danofloxacin mesylate)	[42]
COF-V	In situ synthesis	Alkylbenzenes, chlorobenzenes, phenolic drug, and antiepileptic drug	0.96 mg/mL (methylbenzene)	<2.13 ($n = 3$)	142,265 (methylbenzene)	[43]
COF-TAPB-BPTA	In situ synthesis	Alkylbenzenes, phenols, chlorobenzenes, NSAIDs, and parabens	0.90 mg/mL (methylbenzene)	<2.58 ($n = 3$)	178,260 (methyl-paraben)	This work

LZU-1: Lan Zhou University-1; NSAIDs: non-steroidal anti-inflammatory drugs; TFPB-BD: 1,3,5-tris-(4-formylphenyl)benzene-benzidine; BPF: bisphenol F; Tp: 1,3,5-triformylphloroglucinol; Pa-1: 1,4-phenylenediamine; TAM: tetra(4-aminophenyl)methane; COF-V: vinyl-functionalized COF; TAPB-BPTA: 1,3,5-tris(4-aminophenyl)benzene-2,5-bis(2-propyn-1-yloxy)-1,4-benzenedicarboxaldehyde; –: no data; RSD: relative standard deviation.

3.7. Comparison with other COFs-based OT-CEC columns

The TAPB-BPTA modified capillary was compared with the capillary columns modified by other COFs reported recently, as shown in Table 2 [20,35,39–43]. The in situ room temperature growth method was simple and easy to implement. The TAPB-BPTA modified capillary showed high column capacity and separation efficiency. What is more, the prepared OT columns were quite reproducible. This newly developed COF-based OT column has promising prospects in the chromatographic separation field.

4. Conclusions

A novel kind of COF TAPB-BPTA was successfully modified on the inner surface of the capillary via an in situ growth method at room temperature, and the TAPB-BPTA modified capillary was first used in electrochromatographic separation. The characterization results (SEM, FT-IR, and XRD) confirmed that the TAPB-BPTA was successfully modified on the capillary's inner surface. The dense and uniform TAPB-BPTA coating layer on the capillary's inner wall provided sufficient hydrophobic interactions and π-interactions with the target analytes. Therefore, a typical reverse-phase separation mechanism was obtained. The TAPB-BPTA modified capillary exhibited prominent separation performance toward various hydrophobic compounds. Additionally, the repeatability and stability of the TAPB-BPTA modified column were good. It shows great application potential in separation science.

CRediT author statement

Ning He: Investigation, Data curation, Writing - Original draft preparation; **Zhentao Li:** Conceptualization, Methodology; **Changjun Hu:** Visualization; **Zilin Chen:** Writing - Reviewing and Editing.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpha.2022.06.005.

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